Translated from German by the Ralph McElroy Company, Custom Division
P.O. Box 4828, Austin, TX 78765 USA

Code: 282-36254

FEDERAL REPUBLIC OF GERMANY

GERMAN PATENT OFFICE

PATENT NO. 3,635,427 A1 (Offenlegungschrift)

Int. Cl.[4]:	C 11 D 3/386 C 11 D 3/00 C 11 D 1/12 C 11 D 1/72 //(C 11 D 1/02 3:386 3:37 3:00) (C 11 D 1/66 3:386 3:37 3:00)
Application No.:	P 36 35 427.9
Filing Date:	October 17, 1986
Laid-Open to Public Inspection:	April 23, 1987
Priority:	
Date:	October 18, 1985
Country:	Japan
No.:	232464/85

PHOSPHATE-FREE DETERGENT WITH PECTINASE ACTIVITY

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Examination request has been made according to Section 44, Patent Law.

The invention under consideration concerns a phosphate-free detergent, which is characterized by the content of an enzyme with pectinase activity and possesses a high capacity to remove inorganic soilings from clothes. A preferred phosphate-free detergent contains 0.1 to 30 wt% of the enzyme with pectinase activity, such as polygalacturonase, pectin [sic; pectate] lyase, pectin esterase, 5 to 40 wt% of a surfactant, 5 to 50 wt% of a phosphate-free builder, such as an aluminosilicate, and 0 to 10 wt% of a high-molecular compound, such as carboxymethylcellulose.

Claims

1. Phosphate-free detergent, containing an enzyme with pectinase activity.

2. Phosphate-free detergent according to Claim 1, characterized by the fact that the enzyme with pectinase is polygalacturonase, pectin lyase and/or pectin esterase.

3. Phosphate-free detergent, according to Claim 1 and/or 2, characterized by the fact that the enzyme with pectinase activity contains a value of at least 5 U/mg solids.

4. Phosphate-free detergent according to one of Claims 1 to 3, characterized by the fact that it contains 0.1 to 30 wt% of the enzyme with pectinase activity.

5. Phosphate-free detergent according to one of Claims 1 to 4, characterized by the fact that the detergent is acidic and contains an acidic enzyme with pectinase activity.

6. Phosphate-free detergent according to one of Claims 1 to 4, characterized by the fact that the detergent is alkaline and contains an alkaline enzyme with pectinase activity.

7. Phosphate-free detergent according to one of Claims 1 to 6, characterized by the fact that the detergent contains the enzyme with pectinase activity and another enzyme.

8. Phosphate-free detergent according to one of Claims 1 to 7, characterized by the fact that the detergent contains 0.1 to 30 wt% of the enzyme with pectinase activity, 5 to 40 wt% of a surfactant, 5 to 50 wt% of a phosphate-free builder and 0 to 10 wt% of a high-molecular compound.

9. Phosphate-free detergent according to Claim 8 characterized by the fact that the surfactant is selected from

the following compounds: C_{12} to C_{22}-α-olefinsulfonates, C_8 to C_{18} alkyl ethoxy(1 to 8 mol)sulfates and poly(5 to 20 mol)ethoxylene (C_{10} to C_{18}) alkyl ether.

10. Phosphate-free detergent according to Claims 8 and/or 9, characterized by the fact that it is 0.2 to 10 wt% of the high-molecular compound.

11. Phosphate-free detergent according to Claim 1, characterized by the fact that it contains 5 to 40 wt% of an anionic or nonionic surfactant, 5 to 50 wt% phosphate-free builder, 0.1 to 30 wt% of the enzyme with pectinase activity, 0.1 to 5 wt% alkaline protease and 0.2 to 10 wt% of a high-molecular compound.

Description

The invention under consideration concerns a phosphate-free detergent, which is characterized by the content of an enzyme with pectinase activity. In particular, the invention concerns a detergent that possesses a high capacity to remove inorganic soilings from clothes.

Soilings that dirty clothes are roughly subdivided into degradation products excreted by the human body (fat-like soilings) and soilings from the living environment (inorganic soilings, such as sludge-like dirt).

Such fat-like soilings can be removed to a large extent by using a combination of surface-active agents with a builder, protease or a bleaching agent.

In contrast to this, the removal of the inorganic soilings, which have a behavior different from the fat-like soilings, is more difficult than the removal of the fat-like soilings, because the effects of the surface-active agents are not so remarkable on them. Therefore, there was a great need for the development of a detergent with excellent effect for the removal of inorganic soilings and, in fact, various techniques were proposed. For example, Japanese Patent Publication (Kokai) No. 36,198/1982 states that an agent that contains an aluminosilicate builder and a high concentration of fatty acid soap is effective in the removal of grainy soilings. U.S. Patent Nos. 3,929,678 and 3,925,262 disclose that amphoteric surface-active agents are effective in removing particulate soil (clay). Furthermore, U.S. Patent Nos. 4,228,044 and 4,222,905 describe a combination of a selected cationic surface-active agent and a selected nonionic surface-active agent, which has a high capacity for removing particulate soils (clays). In addition, Japanese Patent Publication No. 3,811/1974 discloses that thiorea dioxide is effective in removing soilings that contain iron compounds (reduction reaction), and Japanese Patent Publication No. 49,279/1984 discloses that the cleaning capacity for sludge-like soilings can be increased by adding cellulase to the detergent.

However, the method disclosed in Japanese Patent Publication (Kokai) No. 36,198/1982 is fraught with difficulties, as the clothes to be cleaned are yellowish because of the soap used and its detergency effect is as low as that of common soap powders. The method mentioned above, in which the amphoteric surface-active agent or a combination of cationic and nonionic surface-active agents is used, also have the difficulty that the effect

of the removal of organic soilings is low, the starting materials cannot be obtained on the market so easily, and the costs are high.

The reducing agents, such as thiourea dioxide, have the difficulty that the discoloring of colored clothing is unavoidable, even if excellent effects can be obtained, if the clothes are immersed in its solution for a long time. The method in which cellulase is used has an excellent effect in removing sludge-like soilings if the soiled cotton clothes are immersed in an aqueous cellulase solution with an optimal pH value, but the problem arises that cellulose deteriorates the strength of cotton fibers (celluloses), which leads to their destruction.

In addition to the difficulties mentioned above, recently the use of a detergent that is free of phosphate builders has been recommended from the standpoint of avoiding eutrophication. Under these circumstances, an increase in detergency for the removal of sludge-like soilings is difficult. More precisely, phosphates, such as sodium tripolyphosphate, have a high dispersion capacity for inorganic substances as one of the effects of the builders and therefore phosphate-containing detergents intrinsically have a high capacity to remove sludge-like soilings. However, zeolite and polycarbonate builders, which were used as a substitute for the phosphate builders, have a capacity for the dispersion of inorganic substances that is lower than that of the phosphates. Therefore, it is technically difficult to increase the capacity of the phosphate-free detergents for the removal of sludge-like soilings.

The invention under consideration is based on the fact that a phosphate-free detergent that contains an enzyme with pectinase

activity has a high capacity for the removal of sludge-like soilings and the aforementioned difficulties can be solved effectively with this detergent.

The goal of the invention therefore is to make available a phosphate-free detergent, which has a great capacity for the removal of sludge-like soilings, without damaging the fibers or exerting a bad influence on the dyed fibers.

Another advantage of the invention under consideration is to be found in making available a detergent that has a high capacity for the removal of fat-like soilings, in addition to the capacity for the removal of sludge-like soilings.

These and other goals and purposes of the invention under consideration can be seen from the following description.

In accordance with the invention, a detergent with an enzyme that has pectinase activity is made available.

Examples of enzymes that have pectinase activity and are available in the invention under consideration comprise the following and their mixtures:

(1) Polygalacturonase, which hydrolyses an α-1,4-glycoside bond of polygalacturonic acid, and (2) pectin lyase, which [hydrolyzes] an α-1,4-glycoside bond of galacturonic acid for the formation of a double bond between C_4 and C_5 with the unreduced end group of uronic acid (hydrolysate) (these enzymes (1) and (2) are subdivided into two groups, that is, a group that acts directly on pectin (substrate) and a group that acts on pectic acid, or alternately, into two groups, that is, a group that acts on the terminal compound of the substrate and a group that breaks the substrate in a statistically random manner), and (3) pectin

esterase, which replaces the methyl galacturonate. It is known that most enzymes that are produced by microorganisms and have pectinase activity contain a mixture of the aforementioned enzymes in a ratio that varies as a function of the microorganism.

The enzyme with pectinase activity, which it is absolutely necessary to have in the invention under consideration, has an activity value of preferably 5 U/mg solid, in particular 10 U/mg solid, independent of the ratio of the enzyme components that comprise the enzyme. The expression "U, Unit" here means a capacity of the enzyme which is needed for the formation of 1 μmol galacturonic acid from the substrate, wherein the activity is determined according to a method which is described in the examples given below.

The detergent of the invention under consideration contains the enzyme with pectinase activity in some desired quantity. Preferably, the quantity is, however, 0.1 to 30 wt% (designated below with %), in particular 0.1 to 10%. The detergent in accordance with the invention is used in quantities of 1.33 to 26.6 g per liter water, so that at least 6.65 units of the enzyme with pectinase activity are contained per liter of wash water.

Because enzymes have their greatest enzymatic effectiveness at an optimal pH value, it is desirable to select an enzyme suitable for the pH of an aqueous solution of the detergent. It is specifically known that enzymes with pectinase activity (designated below as "pectinases") are subdivided into acidic pectinases with optimal pH in the acidic range, alkaline pectinases with an optimal pH in the alkaline pH range and neutral pectinases with an optimal pH in the neutral zone.

Therefore, the acidic and alkaline pectinases are used for the preparation of weakly acidic or alkaline detergents.

Examples of the microorganisms that produce the acidic pectinase and the neutral pectinase comprise:

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An example of the microorganisms that produce the alkaline pectinase is Bacillus P-4-N (according to Japanese Patent Publication No. 6,557/1973).

The following pectinases, which can be obtained commercially and which are produced by these microorganisms, can be used in the invention under consideration:

Sucrase N (Sankyo Co., Ltd.), Ultrapectinex (Novo Industries Co.), Soluble Pectinase (Tanabe Seiyaku Co., Ltd.), Pectinase A (Amano Seiyaku Co., Ltd.), Pectoriase (Seishin Seiyaku Co., Ltd.), Pectinase (Nagase Co., Ltd.), Pectinase SS and Pectinase 3B (Yakult Co., Ltd.).

The detergent in accordance with the invention contains the aforementioned enzyme with pectinase activity as the unavoidable component and, in addition, it can contain the following components:

Surfactants

Anionic Surfactants:
alkylbenzenesulfonates, in which the alkyl group has 8 to 14 carbon atoms;
alkyl sulfates, in which the alkyl group has 8 to 18 carbon atoms;
sulfate salts of ethoxy compounds obtained by the addition of an alcohol in which the alkyl group has 8 to 18 carbon atoms with an average of 1 to 8 mol ethylene oxide;
salts of sulfonated α-olefins with 12 to 22 carbon atoms (mixtures which mainly contain an alkenesulfonate and hydroxyalkanesulfonate);
alkanesulfates, obtained from paraffins with 12 to 22 carbon atoms;
higher fatty acid salts;
salts from the condensed product of a higher fatty acid salt with taurine (N-acylaminosulfonates);
salts of dialkyl sulfosuccinates;
α-sulfofatty acid esters with 12 to 22 carbon atoms and disulfonates of unsaturated fatty acid esters with 12 to 22 carbon atoms.

These salts are preferably alkali metal, ammonium or ethanolamine salts. Magnesium salts of anionic surfactants of the sulfonic acid and sulfate type are also suitable.
Nonionic surfactants:
Polyoxyethylene (C_{10} to C_{18})alkyl ether, polyoxyethylene (C_9 to C_{16})alkylphenol ether, polyoxyethylene fatty acid ester, sorbitan

fatty acid ester, polyoxyethylene ether, sucrose fatty acid ester and fatty acid alkyl amides.

Amphoteric surfactants:

Betaine surfactants, such as lauryldimethylcarboxymethylammonium betaines, alanine surfactants and imidazoline surfactants. In the detergent in accordance with the invention under consideration, the anionic, nonionic and amphoteric surfactants can be used either alone or in the form of mixture of two or more of them.

Builders

The following phosphate-free builders are preferred:

(1) Amino polyacetates, such as nitrilotriacetates, ethylenediaminetetraacetates, iminodiacetates and hydroxyethyliminodiacetates;

(2) amino acids, such as asparaginic acid, glutamic acid and glycine;

(3) salts of dicarboxylic acids, such as oxalic, malonic, succinic, glutaric and adipic acids;

(4) salts and derivatives of hydroxycarboxylic acids, such as glycolic, malic, tartaric, citric, gluconic, glucoronic, mucic, tartronic, carboxymethyltartronic and dicarboxymethyltartaric acids;

(5) itaconic, maleic, fumaric, aconitic, butanetetracarboxcylic, trimesic and pyromellitic acids;

(6) salts of sulfonated carboxylic acids;

(7) aluminosilicates (in particular, zeolite A) with the following general formula:

$Na_2O \cdot Al_2O_3 \cdot nSiO_2 \cdot wH_2O$

wherein n is a number from 1.8 to 3.0 and w, a number from 1 to 6;

(8) reducing alkali metal salts, such as Na_2SO_3;

(9) alkalis and inorganic electrolytes such as silicates, carbonates, sulfates, triethanolamine, monoethanolamine, diethanolamine and triisopropanolamine.

The aforementioned builders (1) to (7) can be used in the form of acids and also in the form of salts with a counterion, such as an alkali metal, for example, sodium or potassium, an alkaline-earth metal, for example, calcium or magnesium, or an alkanolamine with 2 to 3 carbon atoms.

High-molecular compounds

Examples of the high-molecular compounds comprise carboxymethylcellulose (degree of carboxymethylation: 0.2 to 0.9), carboxybutylcellulose (degree of carboxybutylation: 0.2 to 0.9), polyethylene glycol, polyvinyl alcohols (including partially saponified products), polyvinylpyrrolidone, polyacrylic acid, polyitaconic acid, polyfumaric acid, polymaleic acid, polyhydroxyacrylic acid, maleic anhydride/diisobutylene copolymer, maleic anhydride/butadiene copolymer, maleic anhydride/isoamylene copolymer, maleic anhydride/styrene copolymer, maleic anhydride/methyl vinyl ether copolymer, maleic anhydride/venyacetate [sic] copolymer, maleic anhydride/acrylonitrile copolymer, maleic anhydride/acrylic ester copolymer, acrylic acid/styrenesulfonic acid copolymer, itaconic acid/ethylene copolymer, itaconic acid/maleic acid copolymer, itaconic acid/acrylic acid copolymer, ethylene glycol/ethylene terephthalate copolymer, vinylpyrrolidone/vinyl acetate

copolymer, dicarboxymethyl starches and gelatins. Among these, those with a degree of polymerization of 2 to 5,000 are preferred.

Other enzymes

The detergent in accordance with the invention can contain other enzymes in combination with pectinase. Among examples for these enzymes are alkaline protease, lipase and amylase. They can be easily obtained on the market, and they comprise the following commercial products:

I. Alkaline proteases:

Alkalase, Eselase and Savinase (products of Novo Industries Co.)
Maxacal, Maxatase and high-alkaline protease (products of Gist Brocades Co.)
Optimase (a product of Miles Co.)
Alkali protease (a product of Showa Denki K.K.)
Bioprase (a product of Nagase Co., Ltd.)
Prozyme (a product of Amano Seiyaku Co., Ltd.); and
Actinase (a product of Kaken Seiyaku Co., Ltd.); and

II. Lipase:

Termamyl (a product of Novo Co.)
Lipase (a product of Gist Brocades Co.)
Olipase (a product of Nagase Co. Ltd.)
Lipase AP (Amano Seiyaku Co. Ltd.)
Talipase (Tanabe Seiyaku Co. Ltd.)
Godo B-SL (Godo Shusei Co. Ltd.).

Other additives:

The detergent in accordance with the invention can contain other additives, which are usually contained in detergents, such

as a filler, for example, sodium sulfate, a fluorescent optical brightener, a foam regulator, a dye and a fragrance.

A preferred specific embodiment of the detergent containing the aforementioned components comprises 0.1 to 30% of an enzyme with pectinase activity, 5 to 40% of a surfactant, 5 to 50% of a phosphate-free builder and 0 to 10% of a high-molecular compound.

Below, preferred specific embodiments of the invention under consideration are described.

(1) The following combination of the surfactant and the enzyme with pectinase activity is particularly preferred; with this combination, a still higher cleaning capacity for sludge-like soilings can be obtained: a composition containing 5 to 40% of one or more surfactants from the group: (i) C_{12} to C_{22} α-olefinsulfonates, (ii) C_8 to C_{18} alkyl ethoxy(1 to 8 mol)sulfates and (iii) poly(5 to 20 mol)oxyethylene (C_{10} to C_{18}) alkyl ether, 0.1 to 30% of an enzyme with pectinase activity, 5 to 50% of a phosphate-free builder, the remainder auxiliaries for detergents, Glauber's salt and water.

In practice, the following combinations of surfactants are preferred:

1. α-olefinsulfonate/alkylbenzenesulfonate (1/9 to 9/1);
2. alkylbenzenesulfonate/alkyl ethoxy ether sulfate (1/9 to 9/1);
3. alcohol sulfate/alkyl ethoxy ether sulfate (1/9 to 9/1);
4. alkyl ethoxy ether sulfate/polyoxyethylene alkyl ether (1/9 to 9/1);

(2) Another preferred specific embodiment of the detergent contains 0.1 to 30% of an enzyme with pectinase activity and a water-soluble, high-molecular compound. With this combination,

it is possible to attain a high capacity for the removal of sludge-like soilings. Particularly preferred water-soluble high-molecular compounds are carboxymethylcellulose, polyethylene glycol, polyvinyl alcohol, gelatins, polyacrylic acid and its salts, acrylic acid/methyl acrylate copolymer, maleic acid and isoamylene copolymer and maleic acid salts/methyl vinyl ether copolymers. The quantity of water-soluble high-molecular compound is preferably 0.2 to 10%, based on the detergent.

An example of the preferred detergent comprises the aforementioned two components, 5 to 40% of an anionic surfactant or nonionic surfactant, and 5 to 50% of a phosphate-free builder.

(3) Another preferred specific embodiment of the detergent contains 0.1 to 30% of an enzyme with pectinase activity in combination with another enzyme. This agent also has a high capacity for the removal of sludge-like dirts. Another enzyme is preferably alkaline protease, and it is contained in the agent, preferably in a quantity of 0.1 to 5%, in particular 0.3 to 3%.

An example of such a detergent comprises the aforementioned two components, 5 to 40% of an anionic or nonionic surfactant, and 5 to 50% of a phosphate-free builder.

(4) Another preferred specific embodiment of the detergent comprises an enzyme with pectinase activity, alkaline protease and a water-soluble high-molecular compound. This agent has a high capacity for the removal of sludge-like dirts. An example of such a detergent comprises as a base 4 to 40% of an anionic or nonionic surfactant, 5 to 50% of a phosphate-free builder, 0.1 to 30% of an enzyme with pectinase activity, 0.1 to 5% alkaline protease, and 0.2 to 10% of a high-molecular compound.

The detergent in accordance with the invention under consideration can be present in the form of grains, powder, liquid, paste and so forth.

The mechanism for the removal of sludge-like soilings by an enzyme with pectinase activity has not been fully clarified; the inventors, however, suspect the following:

After intensive investigations of the sludge-like dirt surface, which was produced for the purpose of clarifying the reasons for the discoloration with sludge-like dirt, the inventors determined that, surprisingly, an organic substance was found in a large quantity on the surface of the sludge-like soilings. It is suspected that the organic substance brings about an interaction between the fibers of the clothing and the colloid (sludge particles), which makes difficult the removal of the soilings; furthermore, it was surprisingly determined that when using an enzyme with pectinase activity, the latter works together with other components of the detergent, breaking up the interaction and thus exhibiting the excellent effect of the removal of sludge-like soilings.

The invention under consideration will be explained further with the use of the following example, which is not limiting, however.

Examples

A method for the preparation of artificially soiled clothing, washing conditions, washing process and method for the determination of the enzymatic activity in the following examples was as follows:

(1) Preparation of clothing artificially soiled with sludge:

A reddish-yellow soil from the diluvium plateau in Mikatagahara in the Shizuoka Prefecture was dried, pulverized and sized; particles are obtained with an average diameter of approximately 1 m [sic]. The particles were dispersed in ion-exchanged water with ultrasound to form a 1% suspension.

Then, a Yukakyo cotton cloth was brought into contact with the suspension, dried in air for 30 min and dried at 105°C for 30 min. Then the cloth was brushed in order to remove excess soilings. Test cloths with a size of 10 cm x 10 cm were obtained.

(2) Washing conditions, washing process and evaluation process:

The detergent was dissolved in hard water of 3° German hardness; in this way 1 L of a 0.8% aqueous detergent solution was prepared. Five pieces of the artificially soiled cloth were immersed in the aqueous solution at 40° for 1 h, and they were placed directly in a Mini-Mini washer (trade name of Matsushita Electric Industrial Co., Ltd.). The concentration of the detergent was kept under control at 0.133% with tap water; the temperature was set at 25°C, and stirring was carried out for the washing process for 10 min. The cloths were rinsed in running water, ironed and subjected to a reflecting power test.

The degrees of whiteness of the original piece of clothing and the soiled pieces of clothing were measured before and after the washing with a color difference gauge (a product of Nippon Denshoku Co.). The rate of the detergency was calculated according to the following formula:

Detergency rate (%) = (degree of whiteness after the washing) - (degree of whiteness before the washing)/(degree of whiteness

of untreated cloth) - (degree of whiteness before the washing) x 100.

The detergency rate was the average of five pieces of clothing.

(3) Enzymes used and method for the determination of the enzymatic activity:

Enzymes used:

A. Sucrase N (a product of Sankyo Co., Ltd.; prepared by *Coniothyrium diplodiella*), activity: 61.6 U/mg solid.

B. Ultrapectinex SP-L (a product of Novo Industries Co.; produced by *Aspergillus niger*), activity: 54.1 U/mg solid.

C. Pectinase (a product of Nagase Co., Ltd.) activity; 10 U/mg solid.

Method for the determination of the enzymatic activity:

1 mL of an enzyme solution was added to 10 mL of a 0.5% pectic acid solution, which contained an acetate buffer with a pH of 5, and the reaction was carried out at 40°C for 30 min. After the reaction, 6 mL of 0.1N iodine solution were added, and the mixture was allowed to stand in a dark place for 30 min. 6 mL 2M sulfuric acid were added. The iodometric titration was carried out with 0.1N sodium thiosulfate, using starch as an indicator. The quantity of the added titrant was designated as A mL. In a blank test, the enzyme was previously deactivated, and the iodometric titration was carried out in the same way as described above; the quantity of the added titrant was designated as B mL. 1 unit of the activity value gives the capacity of 1 g enzyme for the formation of 1 mol galacturonic acid from pectic

acid. Therefore, the activity value was calculated according to the following formula:

Activity value = (B - A) x 513 x 1/10 x dilution.

1 mg-Eq of iodine reduced corresponds to 0.153 mg-equivalent galacturonic acid. The activities of the aforementioned enzymes A to C were determined according to this method.

Example 1

The detergents (1-1 to 1-4) indicated in Table I were prepared, and their properties were tested. The results and the compositions are summarized in Table I. The quantities of the components of the composition are indicated in wt% and Glauber's salt was added in order to fill the total quantity to 100% (the same is used below).

Table I

(1) Bestandteile		(2) Vergleichsbeispiele 1-1	1-2	(3) Erfindungsgemäß 1-3	1-4
(4) Enzym mit Pectinase-Aktivität	(17) Art	—	C	A	A	B
	(18) Menge	—	2	1	5	5
(5) Natrium-gradkettiges-dodecylbenzolsulfonat		←		20	→	
(6) Natriumsilicat		←		7	→	
(7) Natriumcarbonat		←		7	→	
(8) 4A-Zeolit		←		20	→	
(9) Zitronensäure		←		10	→	
(10) Wasser		←		8	→	
(11) Fluoreszierender Aufheller und Duftstoff		←		1	→	
(12) Glaubersalz		←		(19) Rest	→	
(13) Anzahl der Einheiten von Pectinase pro Gramm Waschmittel		0	200	616	3080	2705
(14) Anzahl der Einheiten von Pectinase pro Liter Waschmittellösung beim Eintauchen verwendet		0	1600	4928	24640	21641
(15) Anzahl der Einheiten von Pectinase in dem Waschwasser		0	267	821	4107	3607
(16) Waschkraft (%)		70	73	74	76	75

Key:
1 Components
2 Comparison examples
3 In accordance with the invention
4 Enzyme with pectinase activity
5 Straight-chain sodium dodecylbenzenesulfonate
6 Sodium silicate
7 Sodium carbonate
8 Zeolite 4A
9 Citric acid
10 Water
11 Fluorescent brightener and fragrance
12 Glauber's salt
13 No. of units of pectinase per gram detergent
14 No. of units of pectinase per liter detergent solution used during the immersion
15 No. of units of pectinase per liter wash water
16 Detergency (%)

17 Type
18 Quantity
19 Remainder

It can be seen from Table I that the detergents in accordance with the invention (1-1 to 1-4) had a great capacity for removing sludge-like soilings.

Example 2

Detergents were prepared with various surfactants, and their properties were tested. The compositions and results are contained in Table II. In Table II, p means an average number of moles of added ethylene oxide (the same is used below).

Table II

(1) Bestandteile	(2) Vergleichsbeispiele	2-1	2-2	(3) Erfindungsgemäß 2-3	2-4	2-5	2-6
(23) Art	—	←		A	→	→	
(4) Enzym mit Pectinase-Aktivität (24) Menge	—	←		5	→	→	
(5) Natrium-α-gradkettiges-dodecylbenzolsulfonat	20	—	10	—	—	10	20
(6) Natrium-α-olefinsulfonat (C_{14} bis C_{18})	—	20	—	—	—	—	—
(7) Alkyl (C_{12} bis C_{14})-ethoxyethersulfat ($\bar{p}$ = 3)	—	—	10	10	20	—	—
(8) Alkylsulfat (C_{14} bis C_{16})	—	—	—	10	—	10	—
(9) Alkyl (C_{12} bis C_{18})-ethoxylat ($\bar{p}$ = 12)	—	—	—	—	15	—	—
(10) Natriumsilicat	7	7	7	7	—	7	7
(11) Natriumcarbonat	7	7	7	7	—	7	7
(12) 4A-Zeolit	20	20	20	20	—	20	20
(13) Zitronensäure	15	15	15	15	5	15	15
(14) Wasser	8	8	8	8	Rest	8	8
(15) Fluoreszierender Aufheller und Duftstoff	1	1	1	1	1.0	1	1
(16) Natrium-p-toluolsulfat	—	—	—	—	2.0	—	—
(17) Ethanol	—	—	—	—	5.0	—	—
(18) Glaubersalz (25)	Rest	Rest	Rest	Rest	—	Rest	Rest
(19) Anzahl von Pectinase-Einheiten pro Gramm Waschmittel	0	←		3080	→	→	
(20) Anzahl von Pectinase-Einheiten pro Liter der beim Eintauchen verwendeten Waschmittellösung	0	←		24640	→	→	
(21) Anzahl von Pectinase-Einheiten pro Liter Waschwasser	0	←		1107	→	→	
(22) Waschkraftrate (%)	70	80	79	78	78	76	76

Key: 1 Components
2 Comparison example
3 In accordance with the invention
4 Enzyme with pectinase activity

5 α-Straight-chain [sic] sodium dodecylbenzenesulfonate
6 Sodium α-olefinsulfonate (C_{14} to C_{18})
7 Alkyl (C_{12} to C_{14}) ethoxy ether sulfate
8 Alkyl sulfate (C_{14} to C_{16})
9 Alkyl (C_{12} to C_{18}) ethoxylate
10 Sodium silicate
11 Sodium carbonate
12 Zeolite 4A
13 Citric acid
14 Water
15 Fluorescent brightener and fragrance
16 Sodium p-toluenesulfate
17 Ethanol
18 Glauber's salt
19 No. of units of pectinase per gram detergent
20 No. of units of pectinase per liter detergent solution used during the immersion
21 No. of units of pectinase per liter wash water
22 Detergency (%)
23 Type
24 Quantity
25 Remainder

From Table II, one can see that among the detergents in accordance with the invention, a composition which contained Na α-olefinsulfonate (a preferred surfactant) alone (2-1) and compositions which contained the same in combination with another preferred surfactant (2-2 to 2-4) had a higher detergency than those of a composition which contained sodium alkylbenzenesulfonate (2-6) or those of a composition which contained both sodium alkylbenzenesulfonate as well as alkyl sulfate (2-5).

Example 3

Detergents with a content of various water-soluble high-molecular compounds were prepared, and their properties were tested. The compositions and results are shown in Table III. An enzyme which was produced by *Bacillus subtilis* (containing a large quantity of pectin lyase; below designated as enzyme D) and alkaline pectinase, produced by Bacillus P-4-N (below, designated as enzyme E) were used in addition to the enzymes A, B and C mentioned in Example 1. In the determination of the enzymatic activity of enzymes D and E, 0.1M glycine-NaOH-NaCl buffer (pH 9) was used instead of the acetate buffer. The unit (titer) was determined as above.

Table III

(1) Bestandteile		(2) Vergleichsbeispiele	(3) Erfindungsgemäß 3-1	3-2	3-3	3-4	3-5	3-6	3-7	3-8	3-9
(4) Enzym mit Pectinase-Aktivität (26)	Art	—	A	A	E	D	B	C	B	B	B
	%	—	5	5	8	10	5	5	5	5	5
(5) Natrium-gradkettiges-dodecylbenzolsulfonat		20	20	20	20	20	20	20	—	10	
(6) Natrium-α-olefinsulfonat (C_{14} bis C_{16})		—	—	—	—	—	—	—	20	—	—
(7) Alkyl (C_{12} bis C_{16})-ethoxysulfat ($\bar{p}$ = 12)		—	—	—	—	—	—	—	—	10	10
(8) Alkylsulfat (C_{14} bis C_{16})		—	—	—	—	—	—	—	—	—	10
(9) Alkyl (C_{12} bis C_{15})-ethoxylat ($\bar{p}$ = 12)		—	—	—	—	—	—	—	—	—	—
(10) Natriumsilicat		←				10					→
(11) Natriumcarbonat		←				10					→
(12) 4A-Zeolit		15	15	10	15	15	10	10	10	10	10
(13) Zitronensäure		5	10	10	5	5	10	10	10	10	10
(14) Polyethylenglycol		—	—	2	—	—	—	—	2	2	2
(15) Natriumpolyacrylat (M = 3000)		—	—	—	2	—	—	—	—	—	—
(16) Carboxymethylzellulose ($\bar{p}$ = 280)		2	—	—	—	2	—	—	—	—	—
(17) Polyvinylalkohol		—	—	—	—	—	2	—	—	—	—
(18) Isoamylen/Maleinsäureanhydrid-Mischpolimer (Natriumsäure : M = 3000)		—	—	—	—	—	—	2	—	—	—
(19) Wasser		←				8					→
(20) Duftstoff		←				1					→
(21) Kilaubersalz		←				(27) Rest					→
(22) Zahl der Einheiten von Pectinase/Gramm		0	3080	3080	500	500	2705	500	2705	2705	2705
(23) Zahl der Einheiten von Pectinase pro Liter Waschmittel verwendet beim Eintauchen		0	24640	24640	4000	4000	21640	4000	21640	21640	21640
(24) Zahl der Einheiten von Pectinase pro Liter Waschwasser		0	4107	4107	667	667	3607	667	3607	3607	3607
(25) Waschkraft (%)		70	76	80	81	83	80	78	85	84	86

Key: 1 Components
2 Comparison examples
3 In accordance with the invention
4 Enzyme with pectinase activity
5 Straight-chain sodium dodecylbenzenesulfonate
6 Sodium α-olefinsulfonate (C_{14} to C_{18})
7 Alkyl (C_{12} to C_{18}) ethoxy sulfate
8 Alkyl sulfate (C_{14} to C_{16})
9 Alkyl (C_{12} to C_{18}) ethoxylate
10 Sodium silicate
11 Sodium carbonate
12 Zeolite 4A
13 Citric acid
14 Polyethylene glycol
15 Sodium polyacrylate (M = 3,000)
16 Carboxymethylcellulose
17 Polyvinyl alcohol
18 Isoamylene/maleic anhydride copolymer (sodium-acid: M = 3000)
19 Water
20 Fragrance
21 Glauber's salt
22 No. of units of pectinase/gram
23 No. of units of pectinase per liter detergent solution used during the immersion
24 No. of units of pectinase per liter wash water
25 Detergency (%)
26 Type
27 Remainder

It can be seen from Table III that among the detergents of the invention under consideration, those which contained a water-soluble high-molecular compound (3-2 to 3-9) had a higher detergency than those which did not contain a water-soluble high-molecular compound (3-1). As water-soluble high-molecular compounds, sodium polyacrylate and carboxymethylcellulose were particularly preferred. It is also obvious that the detergency

power can be increased by a combination of the detergent with a preferred surfactant (3-7 to 3-9).

Example 4

Detergents that contain the combination of an enzyme with pectinase activity with another enzyme (alkaline protease) were produced, and their properties were tested. The results are summarized in Table IV.

Table IV

(1) Bestandteile		(2) Vergleichsbeispiele 4-1	(3) Erfindungsgemäß 4-2	4-3
(4) Enzyme mit Pectinase-Aktivität	(18) Art	—	A	B	A
	%	—	1.0	1.0	1.0
(5) Alkaliprotease (Alkalase von Novo Industries Co.)		1.0	—	1.0	1.0
(6) Natrium-gradkettiges-dodecylbenzolsulfonat		20			
(7) Natriumsilicat		10			
(8) Natriumcarbonat		5			
(9) A-Zeolit		20			
(10) Zitronensäure		5	10	10	10
(11) Wasser		8			
(12) Aufheller und Duftstoff		1			
(13) Glaubersalz		(19) Rest			
(14) Anzahl der Einheiten von Pectinase pro Gramm Waschmittel		0	616	541	616
(15) Anzahl der Einheiten von Pectinase pro Liter Waschmittellösung beim Eintauchen verwendet		0	4928	4328	4928
(16) Anzahl der Einheiten von Pectinase pro Liter Waschwasser		0	821	721	821
(17) Waschkraftrate (%)		70	74	77	77

Key:
1 Components
2 Comparison examples
3 In accordance with the invention
4 Enzyme with pectinase activity
5 Alkaline protease (Alkalase from Novo Industries Co.)
6 Straight-chain sodium dodecylbenzenesulfonate
7 Sodium silicate
8 Sodium carbonate
9 Zeolite 4A
10 Citric acid
11 Water
12 Brightener and fragrance
13 Glauber's salt
14 No. of units of pectinase per gram detergent
15 No. of units of pectinase per liter detergent solution used during immersion
16 No. of units of pectinase per liter wash water

17 Detergency (%)
18 Type activity
19 Remainder

It can be seen from Table IV that the washing capacity can be increased by the combination of pectinase and protease (4-2 and 4-3).

Example 5

Detergents that contain a combination of an enzyme with pectinase activity with alkaline protease and a water-soluble high-molecular compound were prepared and their properties tested. The results are summarized in Table V.

Table V

(1) Bestandteile	(2) Vergleichsbeispiele		(3) Erfindungsgemäß			
		5-1	5-2	5-3	5-4	5-5
(4) Natrium-gradkettiges-dodecyl-benzolsulfonat	←		20			→
(5) Polyethylenglycol	—	2	—	2		—
(6) Natriumpolyacrylat (M: 3000)	—	—	2	—	2	2
(7) Enzym mit Pectinase-Aktivität (20) Art	—	A	B	E	D	A
(20) %	—	1.0	5.0	8	10	1.0
(8) Alkaliprotease	←		1.0			→
(9) Natriumsilicat	←		10			→
(10) Natriumcarbonat	5	5	5	10	11	5
(11) A-Zeolit	←		15			→
(12) Zitronensäure	10	10	10	5	5	10
(13) Duftstoff und fluoreszierender Aufheller	←		1			→
(14) Wasser	←		8			→
(15) Glaubersalz	←		(21) Rest			→
(16) Anzahl der Einheiten von Pectinase pro Gramm Waschmittel	0	3080	2705	500	500	3080
(17) Anzahl der Einheiten von Pectinase pro Liter Waschmittellösung beim Eintauchen verwendet	0	24640	21640	4000	4000	24640
(18) Anzahl der Einheiten von Pectinase pro Liter Waschwasser	0	4107	3607	667	667	4107
(19) Waschkraft (%)	71	83	85	84	84	78

Key:
1 Components
2 Comparison examples
3 In accordance with the invention
4 Straight-chain sodium dodecylbenzenesulfonate
5 Polyethylene glycol
6 Sodium polyacrylate (M: 3,000)
7 Enzyme with pectinase activity
8 Alkaline protease
9 Sodium silicate
10 Sodium carbonate
11 Zeolite 4A

12 Citric acid
13 Fragrance and fluorescent brightener
14 Water
15 Glauber's salt
16 No. of units of pectinase per gram detergent
17 No. of units of pectinase per liter detergent solution used in the immersion
18 No. of units of pectinase per liter wash water
19 Detergency (%)
20 Type
21 Remainder

It can be seen from Table V that the detergency can be considerably increased if protease is added (5-1 to 5-4) to the combination of pectinase and water-soluble high-molecular compounds (5-5).

As can be seen from the description above, the detergent in accordance with the invention has a rather high capacity for the removal of sludge-like soilings, although it is free from a phosphate builder. Another service of this invention lies in the fact that, unlike a cellulase-containing detergent, the fibers are not damaged.

The detergent in accordance with the invention also has a great capacity for the removal of fat-like soilings, in addition to the aforementioned effects, and therefore can be used not only for washing clothing, but also for washing various substances over a wide range.